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Formulation of the Linear Response Theory in Relativistic LAPW Method. Calculation of Forces in Alpha-Pu

A. L. Kutepov

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REPORT

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FORMULATION OF THE LINEAR RESPONSE THEORY IN RELATIVISTIC LAPW METHOD. CALCULATION OF FORCES IN ALPHA-PU

Principal Investigator **A. L. Kutepov**

Abstract

Linear-response (LR) theory in combination with the first-principles band structure codes allows to calculate phonons in an efficient way. In this report a formalism which enables us to apply LR theory within an all-electron framework utilizing the relativistic full-potential linearized augmented plane-wave (RFLAPW) method is presented. As first part, the equations for the calculations of the atomic forces are given and they are used for the calculation of forces in α-Pu. As a second step, a complete set of formulaes for the dynamic matrices calculation is presented.

I. INTRODUCTION

The calculations based on the density-functional theory (the so called first-principles calculations) are now commonly carried out for solid-state systems. Although the basic results of such calculations are the electronic structure and the total energy of the ground state, many other related physical properties can be obtained from them. In particular, the first and the second derivatives of the total energy with respect to the atomic displacements (atomic forces and phonon dispersions correspondingly) can be calculated directly, i.e. without numerical differentiating of the energy.

The important application of the atomic forces consist in the geometry relaxation of the complex crystal structures. While, the relaxation can be accomplished by directly calculating the total energy for different atomic geometries and finding the equilibrium geometry using some fitting procedure, such an approach is not an efficient one, especially for large systems. A better approach is to calculate the atomic forces rather than the total energy since the former gives much more information for using in the process of geometry relaxation.

Accordingly, it is standard in many electronic structure methods to calculate and use atomic forces to relax the coordinates of atoms. However, until quite recently the force calculations were used only with the pseudo-potential approximations and with plane-wave representations for the wave functions, charge density and potential. In the all-electron methods, such as linear-muffin-tin-orbital method (LMTO) and linear-augmented-plane-wave method (LAPW), the atomic force calculations are complicated by the dependence of the basis set on the atomic position. Nevertheless, the formulations of the theory for force calculations in the LMTO[1] and LAPW[2–5] have been given in the last years. All these formulations, however, are non-relativistic (scalar-relativistic) and the application of them to the heavy elements will give some error.

In the present report the fully relativistic generalization of the formulation, developed in [2] is given. This methodology is used to estimate the effect of geometry relaxation on the calculated ground state properties of α-Pu. To be more exact, in the first report on the contract B530324 the calculated total energy of α-Pu as a function of volume had been presented, and the ground state properties had been calculated. However, these calculations had been carried out at a fixed geometry, corresponding to the experimental one at $P = 0$. The crystal structure of α-Pu has, however, many structural parameters, and their dependencies on the volume can be different. Thus, if the geometry relaxation is performed in the calculations, the ground state properties can be different with respect to the ones, calculated at fixed geometry. This question for α-Pu has already been investigated by Sadigh et al..[6] They used both the full potential linear muffin-tin orbital (FPLMTO) and the projector augmented-wave (PAW) methods. The relaxation of the structure in the nonmagnetic PAW treatment increased the atomic volume by 3% and improved agreement with experiment. However, the relaxation of the structure in magnetic PAW treatment decreased the atomic volume and led to some deterioration in agreement with experiment. In the FPLMTO treatment only the parameter c/a was optimized, and the results appeared to be very close to the experiment.

In the present work, only the atomic force calculation has been carried out at each volume. Full geometry relaxation has not been performed, because the RSPFLAPW method is very time-consuming and the above task is much out of our computational resources. Instead of that, the dependence of the calculated forces on the volume have been used to assess the effect of geometry relaxation on the ground state properties of α-Pu, which were corresponded in the first report.

The phonon spectra (lattice dynamics) are essential in many applications and ab-initio calculations of them could provide insight into many problems, such as the construction of the equations of state and the study of the superconducting properties (if the electron-phonon interaction is calculated after the phonon spectrum has been calculated). The most successful approach for the phonon spectra calculations (LR - linear response) has been introduced by Baroni et al..[7] In this approach, the self-consistent response to the external perturbations is obtained by iteration, much as the charge density and potential are obtained in the usual self-consistent band-structure calculations. Similar to the atomic forces calculations, the majority of the linear-response calculations so far employ plane-wave basis functions. The use of a plane-wave basis set simplifies the formalism and implementation. However, plane-wave basis sets are not efficient for many chemical elements with spatially localized distribution of the charge density. With a view towards the applications to such materials, the LMTO[8] and LAPW[9] methods were generalized to include the possibility of phonon spectra calculations.

The present report contain the fully relativistic generalization of the nonrelativistic approach, developed in the Ref.[9]. The equations are given for the non-spin polarized case only, partly because the calculations for the non-magnetic α-U are planned as a first application, and partly because the magnetic case requires some special treatment (the time-reversal symmetry, heavily used in this work, is absent in the magnetic case, and it must be replaced by more general type of symmetry).

The report is organized as follows. In section II the method for atomic forces calculation is presented. The calculational parameters and results of the forces calculations for α-Pu are presented in section III. The relativistic variant of the linear-response theory is presented in section IV and formulaes for dynamical matrix calculation are given in section V. Lastly, in section VI the conclusions and future plans are offered.

II. ALL-ELECTRON RSPFLAPW FORCES

In this section we shall find the general atomic force within the relativistic spin-polarized density-functional formalism. We shall assume that the charge density $n(\boldsymbol{r})$, magnetization $\boldsymbol{m}(\boldsymbol{r})$, effective potential $V_{eff}(\boldsymbol{r})$, and magnetic field $\boldsymbol{B}(\boldsymbol{r})$ are self-consistent. The total energy is given[10] with the equation (in atomic Ridberg units):

$$E[n,\boldsymbol{m}] = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} E_\lambda(\boldsymbol{k}) - \int_\Omega \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) V_{eff}(\boldsymbol{r}) - \int_\Omega \mathrm{d}\boldsymbol{r} \boldsymbol{m}\cdot\boldsymbol{B}(\boldsymbol{r}) + \int_\Omega \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) + \int_\Omega \mathrm{d}\mathbf{r} \int_\Omega \mathrm{d}\boldsymbol{r}' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{\mid \boldsymbol{r}-\boldsymbol{r}' \mid} + E_{xc}[n,\boldsymbol{m}] + E_{nn}, \quad (1)$$

where Ω is the volume of the unit cell of a given solid, $f_{\boldsymbol{k}\lambda}$ are the number of occupation for the one-particle state with wave vector $\boldsymbol{k}$ and with band index λ, and $E_\lambda(\boldsymbol{k})$ indicates the band energy. The term $V_{ext}(\boldsymbol{r})$ designates a scalar external potential, representing the nuclei electrostatic potential. The fifth term is the classical Coulomb energy. The term E_{xc} gives the exchange and correlation energy, which is a functional of $n(\boldsymbol{r})$ and $\boldsymbol{m}(\boldsymbol{r})$, and the last term E_{nn} is an energy of nuclear-nuclear repulsion.

The band energies $E_\lambda(\boldsymbol{k})$ defined from the equality

$$E_\lambda(\boldsymbol{k}) \int_\Omega \mathrm{d}\boldsymbol{r} \Psi_\lambda^\dagger(\boldsymbol{k},\boldsymbol{r}) \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) = \int_\Omega \mathrm{d}\boldsymbol{r} \Psi_\lambda^\dagger(\boldsymbol{k},\boldsymbol{r}) \left[\hat{H}_{kin} + V_{eff}(\boldsymbol{r}) + \beta\widetilde{\boldsymbol{\sigma}}\cdot\boldsymbol{B}\right] \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}), \quad (2)$$

with the Dirac kinetic Hamiltonian $\hat{H}_{kin}$, defined as

$$\hat{H}_{kin} = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + (\beta - I)\frac{c^2}{2}, \tag{3}$$

where c is the velocity of light ($c = 274.074$ in Rydberg units), $\boldsymbol{p}$ is the momentum operator ($\equiv -i\nabla$), and the three operators, $\boldsymbol{\alpha}$, β, and I, denote the standart Dirac 4×4 matrices.

The scalar effective potential $V_{eff}(\boldsymbol{r})$ is defined as

$$V_{eff}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + 2\int_{\Omega} \mathrm{d}\boldsymbol{r'} \frac{n(\boldsymbol{r'})}{\mid \boldsymbol{r} - \boldsymbol{r'} \mid} + \frac{\delta E_{xc}[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}, \tag{4}$$

whereas the effective magnetic field $\boldsymbol{B}(\boldsymbol{r})$ is obtained as

$$\boldsymbol{B}(\boldsymbol{r}) = \frac{\delta E_{xc}[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})]}{\delta \boldsymbol{m}(\boldsymbol{r})}. \tag{5}$$

The charge density, $n(\boldsymbol{r})$, and the magnetization $\boldsymbol{m}(\boldsymbol{r})$, are defined using the Bloch functions $\Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})$ by

$$n(\boldsymbol{r}) = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Psi^\dagger_\lambda(\boldsymbol{k}, \boldsymbol{r}) \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r}), \tag{6}$$

and

$$\boldsymbol{m}(\boldsymbol{r}) = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Psi^\dagger_\lambda(\boldsymbol{k}, \boldsymbol{r}) \beta \widetilde{\boldsymbol{\sigma}} \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r}), \tag{7}$$

respectively. Here, $\widetilde{\boldsymbol{\sigma}}$ denotes the 4×4 matrices, which are composed of the Pauli matrices $\boldsymbol{\sigma}$ as

$$\widetilde{\boldsymbol{\sigma}} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \tag{8}$$

Let us consider the first order correction to the total energy (1) when the crystal is perturbed by the periodic displacement $Q_{t\alpha}$ (t designates the atoms in the unit cell, α is the polarization):

$$\begin{aligned} \delta_{t\alpha} E[n, \boldsymbol{m}] = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \delta_{t\alpha} E_\lambda(\boldsymbol{k}) - \int_\Omega \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) \delta_{t\alpha} V_{eff}(\boldsymbol{r}) - \int_\Omega \mathrm{d}\boldsymbol{r} \boldsymbol{m} \cdot \delta_{t\alpha} \boldsymbol{B}(\boldsymbol{r}) \\ + \int_\Omega \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) \delta_{t\alpha} V_{ext}(\boldsymbol{r}) + \delta_{t\alpha} E_{nn}, \end{aligned} \tag{9}$$

In deriving the above equation we used the self-consistency as well as the equality

$$\delta_{t\alpha} E_{xc}[n, \boldsymbol{m}] = \int_{\Omega} \mathrm{d}\boldsymbol{r} \left[\delta_{t\alpha} n(\boldsymbol{r}) V_{xc}(\boldsymbol{r}) + \delta_{t\alpha} \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}) \right], \tag{10}$$

Also, the term containing the change of the occupation numbers vanishes as follows from the relations

$$\delta_{t\alpha} f_{\boldsymbol{k}\lambda} = \delta(E_F - E_\lambda(\boldsymbol{k}) \delta_{t\alpha} E_F + \frac{\partial f_{\boldsymbol{k}\lambda}}{\partial E_\lambda(\boldsymbol{k})} \delta_{t\alpha} E_\lambda(\boldsymbol{k}) = \delta(E_F - E_\lambda(\boldsymbol{k}) \left[\delta_{t\alpha} E_F - \delta_{t\alpha} E_\lambda(\boldsymbol{k}) \right], \tag{11}$$

and

$$\begin{aligned} \sum_{\boldsymbol{k}\lambda} \delta_{t\alpha} f_{\boldsymbol{k}\lambda} E\lambda(\boldsymbol{k}) &= \sum_{\boldsymbol{k}\lambda} \delta(E_F - E_\lambda(\boldsymbol{k}) \left[\delta_{t\alpha} E_F - \delta_{t\alpha} E_\lambda(\boldsymbol{k}) \right] E_\lambda(\boldsymbol{k}) \\ &= E_F \sum_{\boldsymbol{k}\lambda} \delta(E_F - E_\lambda(\boldsymbol{k}) \left[\delta_{t\alpha} E_F - \delta_{t\alpha} E_\lambda(\boldsymbol{k}) \right] \\ &= E_F \sum_{\boldsymbol{k}\lambda} \delta_{t\alpha} f_{\boldsymbol{k}\lambda} = E_F \delta_{t\alpha} N_{el} = 0, \end{aligned} \tag{12}$$

It is necessary to notice that the first order correction for the coordinate depended variables, consist of two terms:[1] the so called "soft" contribution ($\check{\delta} n$ - for the charge density) and the so called "rigid" term, that goes merely from the fact that our coordinate system is position dependent. Thus, for example (inside the MT-spheres): $\delta n = \check{\delta} n - \nabla n$.

The contribution from the first term in (9) is divided into core and valence terms. For the valence states we have

$$\begin{aligned} \delta_{t\alpha} E_\lambda(\boldsymbol{k}) = \int_{S_t} \mathrm{d}S_\alpha \left[\Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r}) \hat{H}_{kin} \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})|_{MT} - \Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r}) \hat{H}_{kin} (\Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})|_{Int} \right] \\ + \int_{\Omega} \mathrm{d}\boldsymbol{r} \delta_{t\alpha} \Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r}) \left[\hat{H} - E_\lambda(\boldsymbol{k} \right] \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r} + \int_{\Omega} \mathrm{d}\boldsymbol{r} \Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r}) \left[\hat{H} - E_\lambda(\boldsymbol{k} \right] \delta_{t\alpha} \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r}) \\ + \int_{\Omega} \mathrm{d}\boldsymbol{r} |\Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})|^2 \delta_{t\alpha} V_{eff}, \end{aligned} \tag{13}$$

where the surface integral is taken over the boundary of MT-sphere and it represents the relativistic analog to the nonrelativistic contribution[2] from the discontinuity at the sphere boundary.

The core states, being low lying in energy and localized around the nucleus, are described in our approach by neglecting the nonspherical potential and by neglecting the magnetic splitting at all:

$$\left[\hat{H}_{kin} + V^S_{eff}(\boldsymbol{r})\right] \Psi^c_{ti}(\boldsymbol{r}) = E^c_i \Psi^c_{ti}(\boldsymbol{r}), \tag{14}$$

where index i is used for numbering the core levels.

Taking advantage of the fact that the wave functions for the core levels are exact solutions of (14) and that they equal to zero at the sphere boundaries, we arrive to the following equality

$$\delta_{t\alpha} E^c_{ti} = \int_{\Omega_t} \mathrm{d}\boldsymbol{r} |\Psi^c_{ti}(\boldsymbol{r})|^2 \breve{\delta}_{t\alpha} V_{eff} \tag{15}$$

In deriving the above equation we have also taken into account the fact that the integration in (15) is performed only over the MT-sphere, which is shifted itself. So, the "rigid" variation ∇V_{eff} is cancelled for the core levels.

Substituting the Eqs.(13) and (15) in Eq. (9), we arrive to the following expression

$$\begin{aligned} \delta_{t\alpha} E[n, \boldsymbol{m}] = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Big\{ \int_{S_t} \mathrm{d}S_\alpha [\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) \hat{H}_{kin} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{MT} - \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) \hat{H}_{kin} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int}] \\ + \int_\Omega \mathrm{d}\boldsymbol{r} \delta_{t\alpha} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) [\hat{H} - E_\lambda(\boldsymbol{k}] \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + \int_\Omega \mathrm{d}\boldsymbol{r} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) [\hat{H} - E_\lambda(\boldsymbol{k}] \delta_{t\alpha} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \Big\} \\ + \int_{\Omega_t} \mathrm{d}\boldsymbol{r} n_c(\boldsymbol{r}) \nabla_\alpha V_{eff}(\boldsymbol{r}) + \int_{\Omega_t} \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) \delta_{t\alpha} V_{ext}(\boldsymbol{r}) + \delta_{t\alpha} E_{nn}, \end{aligned} \tag{16}$$

To further simplify the above expression, it is necessary to consider explicitly the first variation of the valence wave functions. Keeping in mind the expression[10]

$$\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) = \sum_{\boldsymbol{G}s} A^{\boldsymbol{G}s}_\lambda(\boldsymbol{k}) \Phi_A(\boldsymbol{k}+\boldsymbol{G}, s; \boldsymbol{r}) + \sum_{tn} B^{an}_\lambda(\boldsymbol{k}) \Phi^{an}_B(\boldsymbol{k};\boldsymbol{r}) = \sum_{j'} C^{j'}_\lambda(\boldsymbol{k}) \Phi^{j'}(\boldsymbol{k};\boldsymbol{r}), \tag{17}$$

where the basis functions of all types (local and plane-wave) were unified, we obtain

$$\begin{aligned} \delta_{t\alpha} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{t'} = \sum_{j'} \delta_{t\alpha} C^{j'}_\lambda(\boldsymbol{k}) \Phi^{j'}(\boldsymbol{k};\boldsymbol{r}) \\ + \delta_{tt'} \left[i k_\alpha \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + i \sum_{\boldsymbol{G}s} G_\alpha A^{\boldsymbol{G}s}_\lambda(\boldsymbol{k}) \Phi_A(\boldsymbol{k}+\boldsymbol{G}, s; \boldsymbol{r}) - \nabla_\alpha \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \right], \end{aligned} \tag{18}$$

where the terms inside the square brackets are present only inside the MT-sphere. If we substitute this equality in (16), the contributions with δC are cancelled due to the matrix equation $\sum_{j'}(H_{jj'} - EO_{jj'})C_{j'} = 0$. The contribution from the term $ik_\alpha \Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})$ in (18) is also cancelled and, after some transformations, we arrive to the expression for the forces

$$
\begin{aligned}
F_{t\alpha} = -\delta_{t\alpha} E[n, \boldsymbol{m}] = -\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \\
\times \Bigg\{ -\mathrm{i} \sum_{\boldsymbol{G}s} G_\alpha A_\lambda^{*\boldsymbol{G}s}(\boldsymbol{k}) \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Phi_A^\dagger(\boldsymbol{k}+\boldsymbol{G}, s; \boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\Psi_\lambda(\boldsymbol{k}, \boldsymbol{r}) \\
+\mathrm{i} \sum_{\boldsymbol{G'}s'} G'_\alpha A_\lambda^{\boldsymbol{G'}s'}(\boldsymbol{k}) \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\Phi_A(\boldsymbol{k}+\boldsymbol{G'}, s'; \boldsymbol{r}) \\
- \int_{S_t} \mathrm{d}S_\alpha \Psi_\lambda^\dagger(\boldsymbol{k}, \boldsymbol{r})[\hat{H}_{kin} - E_\lambda(\boldsymbol{k})]\Psi_\lambda(\boldsymbol{k}, \boldsymbol{r})|_{Int} \Bigg\} \\
+ \int_{\Omega_t} \mathrm{d}\boldsymbol{r} V_{eff}(\boldsymbol{r}) \nabla_\alpha n_{val}(\boldsymbol{r}) - \int_{\Omega_t} \mathrm{d}\boldsymbol{r} n_c(\boldsymbol{r}) \nabla_\alpha V_{eff}(\boldsymbol{r}) - \int_{\Omega_t} \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) \delta_{t\alpha} V_{ext}(\boldsymbol{r}) + \delta_{t\alpha} E_{nn}, \quad (19)
\end{aligned}
$$

where the last two terms represent the so called Hellmann-Feynman (HF) contribution to the force, and other terms are contributions that arised from the position dependence of the basis and from the the discontinuity of the basis functions at the MT-spheres.

It is easily to see that the HF contribution is the gradient of the Coulomb potential at nucleus multiplied with its charge Z_t:[2]

$$
\begin{aligned}
F_{t\alpha}^{HF} = - \int_{\Omega_t} \mathrm{d}\boldsymbol{r} n(\boldsymbol{r}) \delta_{t\alpha} V_{ext}(\boldsymbol{r}) + \delta_{t\alpha} E_{nn} \\
= 2Z_t \frac{\partial}{\partial t_\alpha} \left[\int_\Omega \mathrm{d}\boldsymbol{r} \frac{n(\boldsymbol{r})}{|\,\boldsymbol{t} - \boldsymbol{r}\,|} - \sum_{\boldsymbol{R'}\boldsymbol{t'}} \frac{Z_{t'}}{|\,\boldsymbol{t} - \boldsymbol{t'} - \boldsymbol{R'}\,|} \right] = Z_t \nabla_\alpha V^{Coul}(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{t}} \quad (20)
\end{aligned}
$$

The another integrals in (19) have some equivalents in the usual band structure calculations and can be evaluated analogously to them.

III. RESULTS OF CALCULATIONS OF THE FORCES FOR α-PU

The calculations have been performed with the full potential, Dirac relativistic (j, κ) basis, linear-augmented-plane-wave method (RFLAPW+LO)[10] in accordance to the equations described in the section II. The generalized gradient approximation[11] has been used for the

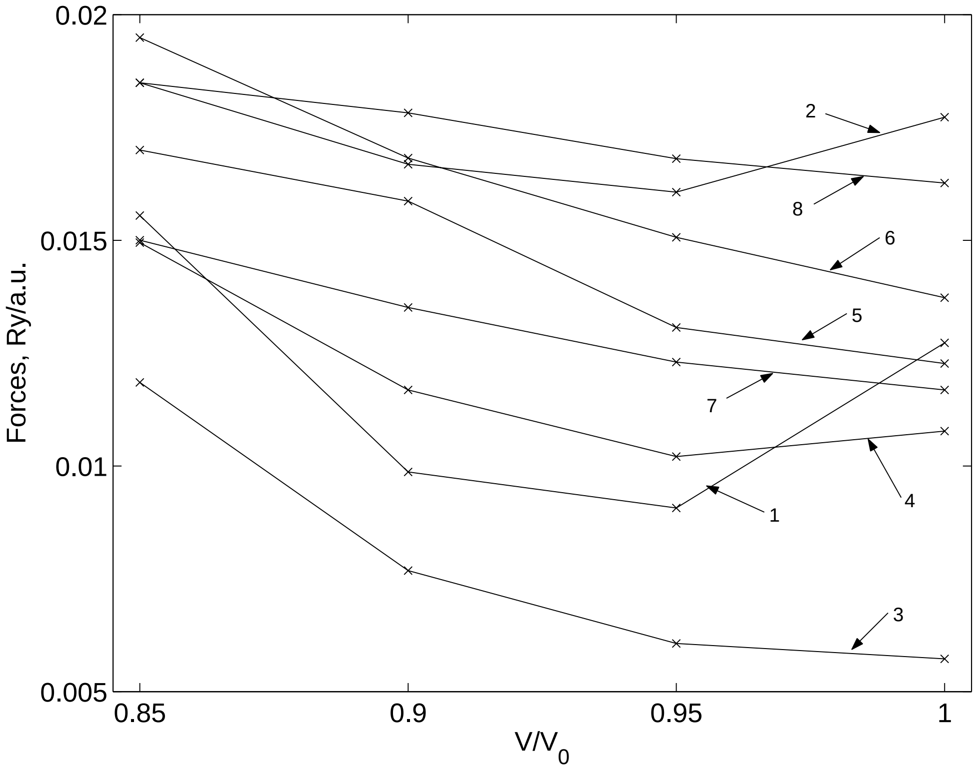

FIG. 1: Absolute values of the atomic forces versus relative volume. V_0 is the experimental equilibrium volume at room temperature. The numbers in the picture indicate the different types of the atoms.

exchange and correlation in this work. The parameters of calculations were the same as in the work [12]. The magnetic structure with the lowest energy (AFM1 - as it had been called in [12]) was chosen for calculating the forces. The abbreviation AFM1 belongs to the magnetic structure of antiferromagnetic type in which the atoms, related by the symmetry operations (equivalent atoms) have the same values and directions of the moments, but the values and directions of the moments on the nonequivalent atoms are generally speaking different. The coordinates of the atoms in the unit cell of α-Pu have been taken from Ref.[13].

The calculations have been carried out at four different volumes with V/V_0 equal to $1.00, 0.95, 0.9$, and 0.85, where V_0 is the experimental volume of α-Pu at room temperature. The results of the calculations are presented in the figures 1 and 2.

In the figure 1 the volume dependence of the forces acted on each of the nonequivalent atoms in unit cell is shown. And in the figure 2 the sum of the absolute values of the forces

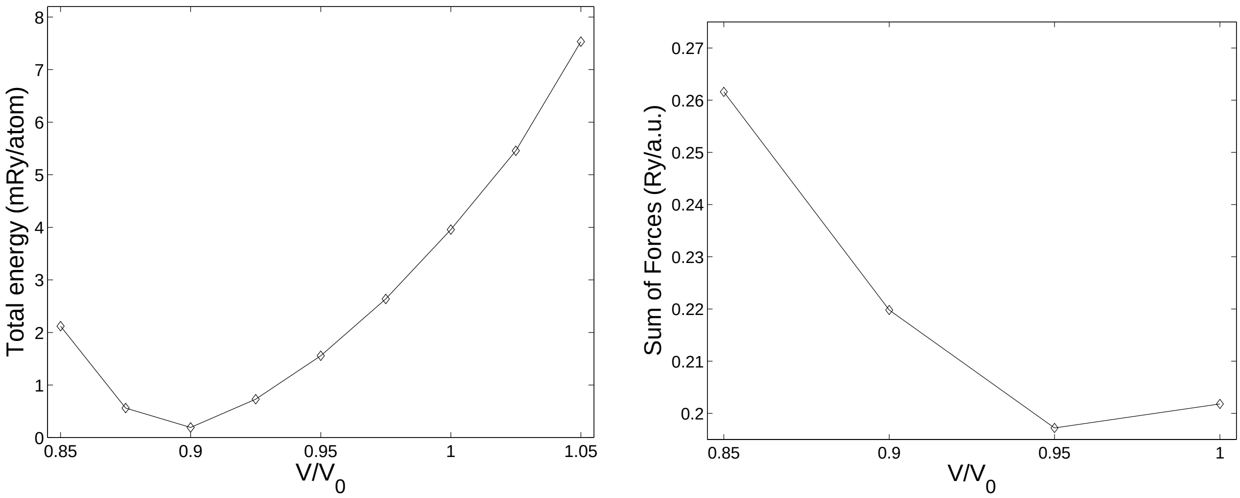

FIG. 2: Total energy (left) and sum of the absolute values of forces over the atoms in the unit cell (right). V_0 is the experimental equilibrium volume at room temperature.

over all the atoms in unit cell is presented versus relative volume (right picture). On the left picture in the figure 2 the total energy as calculated in [13] is shown for convenience.

Two things can be followed from these results. First, it seems from the figure 2 that at the relative volumes larger than near 0.94 the compressibility of the crystal must not be strongly affected by the structure relaxation, because the sum of the forces is practically independent on the volume in this case. Second, at smaller volumes the effect must be present and the smaller volume is the larger must be the lowering of the energy. So, it seems that the relaxation will not expand the calculated equilibrium volume and, thus, will not improve the agreement with the experiment. The same conclusion for magnetic calculations has been given in the Ref.[6] where the full geometry relaxation has been carried out.

It clear, however, that with such an information as presented in the figure 2, one can give only the qualitative conclusions about the effect of geometry relaxation. To give the quantitative conclusions, one needs the full structure relaxation.

IV. DENSITY-FUNCTIONAL LINEAR RESPONSE

We now introduce an external perturbation with the wave vector $\boldsymbol{q}$ to the system:

$$\Delta \boldsymbol{t}_{\boldsymbol{R}}(\boldsymbol{q}) = \boldsymbol{Q}_t \mathrm{e}^{\mathrm{i}\boldsymbol{q}\boldsymbol{R}} + \boldsymbol{Q}_t^* \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\boldsymbol{R}}, \tag{21}$$

where $\boldsymbol{R}$ are the vectors connected with the unit cells of the crystal.

This "phonon" generates a first-order change in the external potential

$$\Delta^1 V_{ext}(\boldsymbol{r}) = \sum_t \boldsymbol{Q}_t \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{qR}} \nabla \frac{2Z_t}{|\boldsymbol{r}-\boldsymbol{t}-\boldsymbol{R}|} + \sum_t \boldsymbol{Q}_t^* \sum_{\boldsymbol{R}} \mathrm{e}^{-\mathrm{i}\boldsymbol{qR}} \nabla \frac{2Z_t}{|\boldsymbol{r}-\boldsymbol{t}-\boldsymbol{R}|} \tag{22}$$

or

$$\Delta^1 V_{ext}(\boldsymbol{r}) = \sum_t \boldsymbol{Q}_t \delta^+ V_{ext}(\boldsymbol{r}) + \sum_t \boldsymbol{Q}_t^* \delta^- V_{ext}(\boldsymbol{r}) \tag{23}$$

The same expression can also be written for the effective potential

$$\Delta^1 V_{eff}(\boldsymbol{r}) = \sum_t \boldsymbol{Q}_t \delta^+ V_{eff}(\boldsymbol{r}) + \sum_t \boldsymbol{Q}_t^* \delta^- V_{eff}(\boldsymbol{r}) \tag{24}$$

The first order change in the charge density (LR-linear response), induced by the perturbation (24) is represented in the same form, i.e. $\Delta^1 n(\boldsymbol{r}) = \sum_t \boldsymbol{Q}_t \delta^+ n(\boldsymbol{r}) + \sum_t \boldsymbol{Q}_t^* \delta^- n(\boldsymbol{r})$ and it is expressed in terms of the one-electron wave functions and their first-order corrections as follows:

$$\begin{aligned} \delta^{\pm} n(\boldsymbol{r}) &= \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \left\{ \delta^{\pm} \Psi_\lambda^\dagger(\boldsymbol{k},\boldsymbol{r}) \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + \Psi_\lambda^\dagger(\boldsymbol{k},\boldsymbol{r}) \delta^{\pm} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \right\} \\ &= 2 \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Psi_\lambda^\dagger(\boldsymbol{k},\boldsymbol{r}) \delta^{\pm} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}), \end{aligned} \tag{25}$$

where we used the time-reversal symmetry. The first order correction $\delta^- \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$ is a Bloch wave with wave vector $\boldsymbol{k}-\boldsymbol{q}$ and it is the solution of the linearized Schödinger-type equation:

$$(H - E_\lambda(\boldsymbol{k}))\delta^- \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + (\delta^- V_{eff} - \delta^- E_\lambda(\boldsymbol{k}))\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) = 0 \tag{26}$$

where the change in the effective potential can be found as

$$\delta^- V(\boldsymbol{r}) = \delta^- V_{ext}(\boldsymbol{r}) + 2\int_\Omega \mathrm{d}\boldsymbol{r'} \frac{\delta^- n(\boldsymbol{r'})}{|\,\boldsymbol{r}-\boldsymbol{r'}\,|} + \frac{\partial V_{xc}}{\partial n} \delta^- n(\boldsymbol{r}) \tag{27}$$

The Eqs. (25)-(27) must be solved selfconsistently. This is analogous to the selfconsistence circle in standard band-structure calculations.

Now we have to provide some details of the solution of the above equation.

A. First order correction to the wave function

In this subsection some explicit formulaes for the first order corrections to the wave functions will be given. First of all, the equation (18) must be modified to take into account the fact that the perturbation is now non periodic, but it has a wave vector $\boldsymbol{q}$. So, in the $\delta^{-}\Psi$ the components with wave vector $\boldsymbol{k}-\boldsymbol{q}$ must only be retained. In the unit cell $\boldsymbol{R}$ and within the MT-sphere of atom t it will be read as

$$\delta^{\pm}_{t'\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Rt} = \sum_{j'} \delta^{\pm}_{t'\alpha'} C^{j'}_{\lambda}(\boldsymbol{k})\Phi^{j'}(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})$$
$$+\delta_{tt'}\mathrm{e}^{\pm \mathrm{i}\boldsymbol{q}\boldsymbol{R}}\Big\{ik_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r}) + i\sum_{\boldsymbol{G}s} G_{\alpha'}A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_{A}(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r}) - \nabla_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})\Big\}, \tag{28}$$

Let us define also the "contracted" forms of the correction. Namely, the one without the gradients in the MT-spheres:

$$\breve{\delta}^{\pm}_{t'\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Rt} = \sum_{j'} \delta^{\pm}_{t'\alpha'} C^{j'}_{\lambda}(\boldsymbol{k})\Phi^{j'}(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})$$
$$+\delta_{tt'}\mathrm{e}^{\pm \mathrm{i}\boldsymbol{q}\boldsymbol{R}}\Big\{ik_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r}) + i\sum_{\boldsymbol{G}s} G_{\alpha'}A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_{A}(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r})\Big\}, \tag{29}$$

the one without the variation of the coefficients:

$$\bar{\delta}^{\pm}_{t'\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Rt} = \delta_{tt'}\mathrm{e}^{\pm \mathrm{i}\boldsymbol{q}\boldsymbol{R}}$$
$$\times\Big\{ik_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r}) + i\sum_{\boldsymbol{G}s} G_{\alpha'}A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_{A}(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r}) - \nabla_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})\Big\}, \tag{30}$$

and the one without the gradients and the variation of the coefficients:

$$\breve{\bar{\delta}}^{\pm}_{t'\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Rt} = \delta_{tt'}\mathrm{e}^{\pm \mathrm{i}\boldsymbol{q}\boldsymbol{R}}\Big\{ik_{\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r}) + i\sum_{\boldsymbol{G}s} G_{\alpha'}A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_{A}(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r})\Big\}, \tag{31}$$

In the interstitial region the expression is simpler

$$\delta^{\pm}_{t'\alpha'}\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Int} = \sum_{\boldsymbol{G}s} \delta^{\pm}_{t'\alpha'} A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_{A}(\boldsymbol{k}-\boldsymbol{q}+\boldsymbol{G},s;\boldsymbol{r}) \tag{32}$$

B. First order variational coefficients

In this subsection some details on the derivation of the first order variational coefficients will be given. In view of the fact, that the perturbation $\delta^- V$ leads to the first order correction $\delta^- \Psi$, which translates with the wave vector $\boldsymbol{k} - \boldsymbol{q}$, it is convenient in the following to use the Hamiltonian (H) and overlap matrices (O) defined in the space spanned by the basis functions at both $\boldsymbol{k}$ and $\boldsymbol{k} - \boldsymbol{q}$ points. For the unperturbed system, the matrix elements $(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{q})$ and $(\boldsymbol{k} - \boldsymbol{q}, \boldsymbol{k})$ vanish, and the eigen vector corresponding to the eigen value $E_\lambda(\boldsymbol{k})$ has $(\boldsymbol{k} - \boldsymbol{q})$-components equal to zero:

$$\left[\begin{pmatrix} H_{\boldsymbol{kk}} & 0 \\ 0 & H_{\boldsymbol{k-qk-q}} \end{pmatrix} - E_\lambda(\boldsymbol{k}) \begin{pmatrix} O_{\boldsymbol{kk}} & 0 \\ 0 & O_{\boldsymbol{k-qk-q}} \end{pmatrix} \right] \begin{vmatrix} C_\lambda(\boldsymbol{k}) \\ 0 \end{vmatrix} = 0 \tag{33}$$

When a perturbation with the wave vector $\boldsymbol{k} - \boldsymbol{q}$ is added to the unperturbed system, the Hamiltonian and overlap matrices are modified in the elements $(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{q})$ and $(\boldsymbol{k} - \boldsymbol{q}, \boldsymbol{k})$. Linearizing Eq.(33), we find

$$\begin{aligned} &\left[\begin{pmatrix} \delta^- H_{\boldsymbol{kk}} & \delta^- H_{\boldsymbol{kk-q}} \\ \delta^- H_{\boldsymbol{k-qk}} & \delta^- H_{\boldsymbol{k-qk-q}} \end{pmatrix} - E_\lambda(\boldsymbol{k}) \begin{pmatrix} \delta^- O_{\boldsymbol{kk}} & \delta^- O_{\boldsymbol{kk-q}} \\ \delta^- O_{\boldsymbol{k-qk}} & \delta^- O_{\boldsymbol{k-qk-q}} \end{pmatrix} \right] \begin{vmatrix} C_\lambda(\boldsymbol{k}) \\ 0 \end{vmatrix} \\ &= - \left[\begin{pmatrix} H_{\boldsymbol{kk}} & 0 \\ 0 & H_{\boldsymbol{k-qk-q}} \end{pmatrix} - E_\lambda(\boldsymbol{k}) \begin{pmatrix} O_{\boldsymbol{kk}} & 0 \\ 0 & O_{\boldsymbol{k-qk-q}} \end{pmatrix} \right] \begin{vmatrix} 0 \\ \delta^- C_\lambda(\boldsymbol{k}) \end{vmatrix} \\ &\qquad + \delta^- E_\lambda(\boldsymbol{k}) \begin{pmatrix} O_{\boldsymbol{kk}} & 0 \\ 0 & O_{\boldsymbol{k-qk-q}} \end{pmatrix} \begin{vmatrix} C_\lambda(\boldsymbol{k}) \\ 0 \end{vmatrix} \end{aligned} \tag{34}$$

From the above system, one can find the first-order eigenvalue:

$$\delta^- E_\lambda(\boldsymbol{k}) = \sum_{jj'} C_\lambda^{*j}(\boldsymbol{k}) \left[\delta^- H_{\boldsymbol{kk}}^{jj'} - E_\lambda(\boldsymbol{k}) \delta^- O_{\boldsymbol{kk}}^{jj'} \right] C_\lambda^{j'}(\boldsymbol{k}), \tag{35}$$

which vanishes except for $\boldsymbol{q} = 0$.

From this point we will suppose that $\boldsymbol{q} \neq 0$ in our considerations. The case with exactly $\boldsymbol{q} = 0$ can be treated in parallel with the degenerate case, as indicated in Ref.[9]. The particular formulaes for the degenerate case will be given with special consideration further.

From Eq.(34), one can also obtain the equation for the first-order variational coefficients:

$$\sum_{j'} \left[H^{jj'}_{\boldsymbol{k-qk-q}} - E_\lambda(\boldsymbol{k}) O^{jj'}_{\boldsymbol{k-qk-q}} \right] \delta^- C^{j'}_\lambda(\boldsymbol{k})$$

$$= - \sum_{j'} \left[\delta^- H^{jj'}_{\boldsymbol{k-qk}} - E_\lambda(\boldsymbol{k}) \delta^- O^{jj'}_{\boldsymbol{k-qk}} \right] C^{j'}_\lambda(\boldsymbol{k}) \tag{36}$$

Expanding $\delta^- C_\lambda(\boldsymbol{k})$ in (36) over the full set of the eigen vectors of the generalized eigen value problem $(H_{\boldsymbol{k-q},\boldsymbol{k-q}}; O_{\boldsymbol{k-q},\boldsymbol{k-q}})$, we have (writing down the indexes explicitly):

$$\delta^-_{t'\alpha'} C_\lambda(\boldsymbol{k}) = \sum_\mu \frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) - E_\lambda(\boldsymbol{k}) \bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k}) - E_\mu(\boldsymbol{k-q})} C_\mu(\boldsymbol{k-q}) \tag{37}$$

where

$$\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) = \sum_{jj'} C^{*j}_\mu(\boldsymbol{k-q}) \delta^-_{t'\alpha'} H^{jj'}_{\boldsymbol{k-qk}} C^{j'}_\lambda(\boldsymbol{k})$$

$$= \int_{\Omega_{t'}} \mathrm{d}\boldsymbol{r} \left[\bar{\delta}^-_{t'\alpha'} \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \hat{H} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \hat{H} \bar{\delta}^-_{t'\alpha'} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \right]$$

$$+ \int_\Omega \mathrm{d}\boldsymbol{r} \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \delta^-_{t'\alpha'} V_{eff}(\boldsymbol{r}) \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$$

$$+ \int_{S_{t'}} \mathrm{d}\boldsymbol{S} \left[\Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \hat{H}_{kin} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{MT} - \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \hat{H}_{kin} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int} \right] \tag{38}$$

and

$$\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) = \sum_{jj'} C^{*j}_\mu(\boldsymbol{k-q}) \delta^-_{t'\alpha'} O^{jj'}_{\boldsymbol{k-qk}} C^{j'}_\lambda(\boldsymbol{k})$$

$$= \int_{\Omega_{t'}} \mathrm{d}\boldsymbol{r} \left[\bar{\delta}^-_{t'\alpha'} \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) + \Psi^\dagger_\mu(\boldsymbol{k-q},\boldsymbol{r}) \bar{\delta}^-_{t'\alpha'} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \right] \tag{39}$$

Making use of the time-reversal symmetry and the hermiticity of the Hamiltonian and overlap matrices, it can be proved that both $\bar{H}_{\mu\lambda}(\boldsymbol{k})$ and $\bar{O}_{\mu\lambda}(\boldsymbol{k})$ have the property

$$\bar{H}^{t'\alpha'}_{\mu\lambda}(-\boldsymbol{k}+\boldsymbol{q}) = \bar{H}^{t'\alpha'}_{\lambda\mu}(\boldsymbol{k}) \tag{40}$$

In the equations (38) and (39) there are the gradients of the effective potential and the gradients of the basis functions. Thus, they are not very convenient for the practical calculations. However, by using the Gauss theorem, these equation can be simplified:

$$
\begin{aligned}
\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) - E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) = \int_{\Omega_{t'}} \mathrm{d}\boldsymbol{r}\Big[&\bar{\breve{\delta}}^{-}_{t'\alpha'}\Psi^\dagger_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})(\hat{H}-E_\lambda(\boldsymbol{k}))\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \\
&+\Psi^\dagger_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})(\hat{H}-E_\lambda(\boldsymbol{k}))\bar{\breve{\delta}}^{-}_{t'\alpha'}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})\Big] \\
&+\int_\Omega \mathrm{d}\boldsymbol{r}\Psi^\dagger_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\breve{\delta}^{-}_{t'\alpha'}V_{eff}(\boldsymbol{r})\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \\
-\int_{S_{t'}} &\mathrm{d}S_\alpha\Psi^\dagger_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})[V_{eff}-E_\lambda(\boldsymbol{k})]\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \\
&-\int_{S_{t'}} \mathrm{d}S_\alpha\Psi^\dagger_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\hat{H}_{kin}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int}
\end{aligned}
\tag{41}
$$

In the above equation the gradients are absent.

C. Construction $\delta^- n$

Using (28) in (25) we have for the linear response inside the MT-spheres:

$$
\begin{aligned}
\delta^{-}_{t'\alpha'}n(\boldsymbol{r})|_{\boldsymbol{t}} = 2\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\Big\{&\sum_{j'}\delta^{-}_{t'\alpha'}C^{j'}_\lambda(\boldsymbol{k})\Phi^{j'}(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r}) \\
+\mathrm{i}\delta_{tt'}\Big[\sum_{\boldsymbol{G'}s'}(G')_{\alpha'}A^{\boldsymbol{G'}s'}_{\lambda'}(\boldsymbol{k})\Phi_A(\boldsymbol{k}+\boldsymbol{G'},s';\boldsymbol{r}) &+ k_{\alpha'}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})\Big] \\
&-\delta_{tt'}\nabla_{\alpha'}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})\Big\},
\end{aligned}
\tag{42}
$$

and in the interstitial:

$$
\delta^{-}_{t'\alpha'}n(\boldsymbol{r}) = 2\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\sum_{\boldsymbol{G'}s'}\delta^{-}_{t'\alpha'}A^{\boldsymbol{G'}s'}_{\lambda'}(\boldsymbol{k})\Phi_A(\boldsymbol{k}-\boldsymbol{q}+\boldsymbol{G'},s';\boldsymbol{r}) \tag{43}
$$

It is followed from (42) that indeed we can write for the linear response within the spheres:

$$
\delta^{-}_{t'\alpha'}n(\boldsymbol{r})|_{\boldsymbol{t}} = \breve{\delta}^{-}_{t'\alpha'}n(\boldsymbol{r}) - \delta_{tt'}\nabla_{\alpha'}n(\boldsymbol{r}), \tag{44}
$$

The expressions (42) and (43) are valid if no degeneracy occurs in the calculations. If the valence state $(\mu,\boldsymbol{k}-\boldsymbol{q})$ is degenerate with the state $(\lambda,\boldsymbol{k})$, it cannot be calculated in the perturbative expression (37). Let us consider such a case with more details. Using (37), we may rewrite (43) or the part of (42) with $\delta^- C$ as follows (we consider only the states $(\mu, \boldsymbol{k}-\boldsymbol{q})$ with $E_\mu(\boldsymbol{k}-\boldsymbol{q}) = E_\lambda(\boldsymbol{k})$):

$$
\begin{aligned}
&2\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\sum_{j'}\sum_{\mu(E^{\boldsymbol{k}-\boldsymbol{q}}_\mu=E^{\boldsymbol{k}}_\lambda)}\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})}C^{j'}_\mu(\boldsymbol{k}-\boldsymbol{q})\Phi^{j'}(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})\\
&=2\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\sum_{\mu(E^{\boldsymbol{k}-\boldsymbol{q}}_\mu=E^{\boldsymbol{k}}_\lambda)}\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})}\Psi_\lambda(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\\
&=\text{(considering explicitly the states } (\mu,-\boldsymbol{k}+\boldsymbol{q}))\\
&\sum_{\boldsymbol{k}\lambda}\sum_{\mu(E^{\boldsymbol{k}-\boldsymbol{q}}_\mu=E^{\boldsymbol{k}}_\lambda)}\Bigg\{f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})}\Psi_\lambda(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\\
&+f_{-\boldsymbol{k}+\boldsymbol{q}\mu}\Psi^\dagger_\mu(-\boldsymbol{k}+\boldsymbol{q},\boldsymbol{r})\frac{\bar{H}^{t'\alpha'}_{\lambda\mu}(-\boldsymbol{k}+\boldsymbol{q})-E_\mu(-\boldsymbol{k}+\boldsymbol{q})\bar{O}^{t'\alpha'}_{\lambda\mu}(-\boldsymbol{k}+\boldsymbol{q})}{E_\mu(-\boldsymbol{k}+\boldsymbol{q})-E_\lambda(-\boldsymbol{k})}\Psi_\mu(-\boldsymbol{k},\boldsymbol{r})\Bigg\}\\
&=\text{(making use of the time-reversal symmetry and property (40))}\\
&\sum_{\boldsymbol{k}\lambda}\sum_{\mu(E^{\boldsymbol{k}-\boldsymbol{q}}_\mu=E^{\boldsymbol{k}}_\lambda)} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\Psi_\lambda(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\Bigg\{\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})}\\
&+\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\mu(\boldsymbol{k}-\boldsymbol{q})-E_\lambda(\boldsymbol{k})}\Bigg\}\\
&=-\sum_{\boldsymbol{k}\lambda}\sum_{\mu(E^{\boldsymbol{k}-\boldsymbol{q}}_\mu=E^{\boldsymbol{k}}_\lambda)} f_{\boldsymbol{k}\lambda}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\bar{O}_{\mu\lambda}(\boldsymbol{k})\Psi_\lambda(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})
\end{aligned}
\tag{45}
$$

Equation (45) thus states that the coefficient in (37) for the degenerate levels must be changed by $-\frac{1}{2}\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})$

D. Construction $\delta^- V_{eff}$

The first order potentials consist of two parts: Coulomb and exchange-correlation. The exchange-correlation part can be evaluated directly:

$$
\delta^-_{t'\alpha'}V_{xc}(\boldsymbol{r}) = \frac{\partial V_{xc}}{\partial n}\delta^-_{t'\alpha'}n(\boldsymbol{r}), \tag{46}
$$

where we supposed the local density approximation (LDA).

Within the MT-spheres it is convenient to separate the term with the gradient of the potential:

$$\delta^{-}_{t'\alpha'}V_{xc}(\boldsymbol{r})|_{\boldsymbol{R}t} = \frac{\partial V_{xc}}{\partial n}[\breve{\delta}^{-}_{t'\alpha'}n(\boldsymbol{r}) - \delta_{tt'}\mathrm{e}^{-\mathrm{i}\boldsymbol{qR}}\nabla_{\alpha'}n(\boldsymbol{r})] = \breve{\delta}^{-}_{t'\alpha'}V_{xc}(\boldsymbol{r}) - \delta_{tt'}\mathrm{e}^{-\mathrm{i}\boldsymbol{qR}}\nabla_{\alpha'}V_{xc}(\boldsymbol{r}) \quad (47)$$

The first order Coulomb potentials can be evaluated similar to the periodic potential[5] of the unperturbed crystal. To calculate them in the interstitial region, we rewrite the Coulomb terms in (27) as follows:

$$\delta^{-}_{t'\alpha'}V_{ext}(\boldsymbol{r}) + 2\int_{\Omega}\mathrm{d}\boldsymbol{r'}\frac{\delta^{-}_{t'\alpha'}n(\boldsymbol{r'})}{\mid \boldsymbol{r}-\boldsymbol{r'}\mid} = 2\int_{\Omega}\mathrm{d}\boldsymbol{r'}\frac{\delta^{-}_{t'\alpha'}n_{Int}(\boldsymbol{r'})}{\mid \boldsymbol{r}-\boldsymbol{r'}\mid}$$
$$+2\sum_{\boldsymbol{R}t}\left[\int_{\Omega_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{r'}\frac{(\delta^{-}_{t'\alpha'}n_{MT}(\boldsymbol{r'}) - \delta^{-}_{t'\alpha'}n_{Int}(\boldsymbol{r'}))}{\mid \boldsymbol{r}-\boldsymbol{r'}\mid} - \mathrm{e}^{-\mathrm{i}\boldsymbol{qR}}\frac{\partial}{\partial t'_{\alpha'}}\frac{Z_t}{\mid \boldsymbol{r}-\boldsymbol{R}-\boldsymbol{t}\mid}\right] \quad (48)$$

All first order variations that present in the sum over MT-spheres in (48) contribute to the interstitial first order potential only via their multipoles, which are defined as

$$\int_{\Omega_t}\mathrm{d}\boldsymbol{r'}(r')^l\bar{Y}_{lm}(\mathrm{r})\left[\delta^{-}_{\mathrm{t'}\alpha'}\mathrm{n_{MT}}(\mathrm{r'}) - \delta^{-}_{\mathrm{t'}\alpha'}\mathrm{n_{Int}}(\mathrm{r'})\right] - \mathrm{Z_t}\delta_{\mathrm{l},1}\begin{cases}\delta_{m,1}, \alpha'=x\\ \delta_{m,-1}, \alpha'=y\\ \delta_{m,0}, \alpha'=z\end{cases}, \quad (49)$$

where $\bar{Y}_{lm}$ are real spherical functions.

So, we can replace these variations by smooth functions that are zero outside the spheres and have multipoles equal to multipoles (49) of the true functions. A convenient choice is to use a polynomial form[5]

$$\tilde{n}_t(\boldsymbol{r}) = \sum_{lm} Q_{lm}\frac{1}{S_t^{l+3}}\left(\frac{r}{S_t}\right)^l\left(1-\frac{r^2}{S_t^2}\right)^N\bar{Y}_{lm}(\boldsymbol{r}), \quad (50)$$

where S_t is radius of the sphere.

This form has $(N-1)$ continuous derivatives and an analytic Fourier transform. The corresponding multipole moments are

$$Q_{lm}\frac{2^N N!(2l+1)!!}{(2l+2N+3)!!} \quad (51)$$

From (49) and (51) we can find the values Q_{lm}. Once this is done, we can determine the Fourier transform $\delta^{-}\tilde{n}_{\boldsymbol{G}}$ of these smooth functions and rewrite the Eq.(48) as following

$$2\int_\Omega \mathrm{d}\boldsymbol{r'}\frac{\sum_{\boldsymbol{G}}\delta^-_{t'\alpha'}n_{\boldsymbol{G}}\mathrm{e}^{\mathrm{i}(\boldsymbol{G}-\boldsymbol{q})\boldsymbol{r'}}}{\mid \boldsymbol{r}-\boldsymbol{r'}\mid}+2\int_\Omega \mathrm{d}\boldsymbol{r'}\frac{\sum_{\boldsymbol{G}}\delta^-_{t'\alpha'}\tilde{n}_{\boldsymbol{G}}\mathrm{e}^{\mathrm{i}(\boldsymbol{G}-\boldsymbol{q})\boldsymbol{r'}}}{\mid \boldsymbol{r}-\boldsymbol{r'}\mid}$$
$$=\sum_{\boldsymbol{G}}\frac{8\pi(\delta^-_{t'\alpha'}n_{\boldsymbol{G}}+\delta^-_{t'\alpha'}\tilde{n}_{\boldsymbol{G}})}{\mid \boldsymbol{G}-\boldsymbol{q}\mid^2}\mathrm{e}^{\mathrm{i}(\boldsymbol{G}-\boldsymbol{q})\boldsymbol{r}}=\sum_{\boldsymbol{G}}\delta^-_{t'\alpha'}V^{Coul}_{\boldsymbol{G}}\mathrm{e}^{\mathrm{i}(\boldsymbol{G}-\boldsymbol{q})\boldsymbol{r}} \tag{52}$$

Having determined the first order Coulomb potential in the interstitial region, we can proceed with the derivation of it within the MT-spheres. To do that we must to integrate Poisson's equation in each sphere with true first order charge density. Since we have already become the first order Coulomb potential in the interstitial region, the boundary condition on the surfaces of the spheres is known. Writing the gradient of the Coulomb potential explicitly, we have for the first order Coulomb potential within MT-sphere:

$$\delta^-_{t'\alpha'}V^{Coul}_{lm}(\boldsymbol{r})|_t=-\delta_{tt'}\nabla_{\alpha'}V^{Coul}(\boldsymbol{r})$$
$$+\sum_{lm}\frac{8\pi\bar{Y}_{lm}}{2l+1}\left[\frac{1}{r^{l+1}}\int_0^r(r')^{l+2}\breve{\delta}^-_{t'\alpha'}n_{lm}(r')\mathrm{dr'}+r^l\int_r^{S_t}\frac{\breve{\delta}^-_{t'\alpha'}n_{lm}(r')}{(r')^{l-1}}\mathrm{dr'}\right]$$
$$+\sum_{lm}\bar{V}_{lm}\left(\frac{r}{S_t}\right)^l \tag{53}$$

The coefficients $\bar{V}_{lm}$ are defined from the condition that the above expression is equal to the interstitial first order Coulomb potential (52) on the surface of the sphere.

V. DYNAMICAL MATRIX

To obtain an explicit expression for the dynamical matrix we consider the second order correction to the total energy after the perturbation (21) has been introduced to the crystal:

$$\Delta^2E_{tot}=\frac{1}{2N}\sum_{\boldsymbol{R}t\alpha}\sum_{\boldsymbol{R'}t'\alpha'}\frac{\partial^2E_{tot}}{\partial t_{\boldsymbol{R}\alpha}\partial t_{\boldsymbol{R'}\alpha'}}\Delta\boldsymbol{t_R}(\boldsymbol{q})\Delta\boldsymbol{t'_{R'}}(\boldsymbol{q}) \tag{54}$$

Defining the force matrix

$$V_{\boldsymbol{R}t\alpha;\boldsymbol{R'}t'\alpha'}=\frac{\partial^2E_{tot}}{\partial t_{\boldsymbol{R}\alpha}\partial t_{\boldsymbol{R'}\alpha'}}, \tag{55}$$

we have

$$\Delta^2 E_{tot} = \frac{1}{2}\sum_{t\alpha}\sum_{t'\alpha'}\left[Q_{t\alpha}Q^*_{t'\alpha'}\sum_{\boldsymbol{P}} V_{0t\alpha;\boldsymbol{P}t'\alpha'}\mathrm{e}^{-\mathrm{i}\boldsymbol{qP}} + Q^*_{t\alpha}Q_{t'\alpha'}\sum_{\boldsymbol{P}} V_{0t\alpha;\boldsymbol{P}t'\alpha'}\mathrm{e}^{\mathrm{i}\boldsymbol{qP}}\right]$$
$$= \sum_{t\alpha;t'\alpha'}\sqrt{m_t m_{t'}}Q_{t\alpha}Q^*_{t'\alpha'}D_{t\alpha;t'\alpha'}(\boldsymbol{q}), \qquad (56)$$

where we used the standard definition of the dynamical matrix through the force matrix

$$D_{t\alpha;t'\alpha'}(\boldsymbol{q}) = \sum_{\boldsymbol{P}} V_{0t\alpha;\boldsymbol{P}t'\alpha'}\mathrm{e}^{-\mathrm{i}\boldsymbol{qP}} \qquad (57)$$

From Eq.(56) we see, that

$$D_{t\alpha;t'\alpha'}(\boldsymbol{q}) = \frac{1}{\sqrt{m_t m_{t'}}}\frac{\partial^2 E_{tot}}{\partial Q_{t\alpha}\partial Q^*_{t'\alpha'}} \qquad (58)$$

The first order derivative can be obtained analogously to the derivation of the Eq. (19) in the case $\boldsymbol{q} = 0$

$$\frac{\partial E_{tot}}{\partial Q_{t\alpha}} = \sum_{\boldsymbol{R}}\mathrm{e}^{\mathrm{i}\boldsymbol{qR}}\Big[\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}$$
$$\{-\mathrm{i}\sum_{\boldsymbol{G}s}\boldsymbol{G}A^{*\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\int_{\Omega_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{r}\Phi^{\dagger}_{A}(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r})[\hat{H}-E_{\lambda}(\boldsymbol{k})]\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})$$
$$+\mathrm{i}\sum_{\boldsymbol{G'}s'}\boldsymbol{G'}A^{\boldsymbol{G'}s'}_{\lambda}(\boldsymbol{k})\int_{\Omega_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{r}\Psi^{\dagger}_{\lambda}(\boldsymbol{k},\boldsymbol{r})[\hat{H}-E_{\lambda}(\boldsymbol{k})]\Phi_{A}(\boldsymbol{k}+\boldsymbol{G'},s';\boldsymbol{r})$$
$$-\int_{S_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{S}\Psi^{\dagger}_{\lambda}(\boldsymbol{k},\boldsymbol{r})[\hat{H}_{kin}-E_{\lambda}(\boldsymbol{k})]\Psi_{\lambda}(\boldsymbol{k},\boldsymbol{r})|_{Int}\}$$
$$-\int_{\Omega_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{r}V_{eff}(\boldsymbol{r})\nabla n_{val}(\boldsymbol{r}) + \int_{\Omega_{\boldsymbol{R}t}}\mathrm{d}\boldsymbol{r}n_c(\boldsymbol{r})\nabla V_{eff}(\boldsymbol{r}) - Z_t\nabla_{\alpha}V_{coul}(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{R}+\boldsymbol{t}}\Big] \qquad (59)$$

Let us now consider the second variation for each term in (59) separately.

A. Hellman-Feynman contribution to the dynamical matrice

The second variation of the HF contribution (20) gives

$$\sqrt{m_t m_{t'}}D^{HF}_{t\alpha;t'\alpha'}(\boldsymbol{q}) = -Z_t\nabla_{\alpha}\delta^{-}_{t'\alpha'}V_{coul}(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{t}} = -Z_t\left[\nabla_{\alpha}\breve{\delta}^{-}_{t'\alpha'}V_{coul}(\boldsymbol{r}) - \delta_{tt'}\nabla_{\alpha}\nabla_{\alpha'}V_{coul}(\boldsymbol{r})\right]|_{\boldsymbol{r}=\boldsymbol{t}} \qquad (60)$$

B. Core contribution to the dynamical matrice

In deriving the formula for the core contribution it is important to keep in mind that the corresponding first order contribution in (59) is depended on the position of the MT-sphere. Thus,

$$\sqrt{m_t m_{t'}} D^c_{t\alpha;t'\alpha'}(\boldsymbol{q}) = \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Big[\Big(\breve{\delta}^-_{t'\alpha'} n_c(\boldsymbol{r}) - \delta_{tt'} \nabla_{\alpha'} n_c(\boldsymbol{r}) \Big) \nabla_\alpha V_{eff}(\boldsymbol{r})$$
$$+ n_c(\boldsymbol{r}) \nabla_\alpha \Big(\breve{\delta}^-_{t'\alpha'} V_{eff}(\boldsymbol{r}) - \delta_{ta'} \nabla_{\alpha'} V_{eff}(\boldsymbol{r}) \Big) \Big]$$
$$+ \delta_{tt'} \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \nabla_{\alpha'} \left[n_c(\boldsymbol{r}) \nabla_\alpha V_{eff}(\boldsymbol{r}) \right]$$
$$= \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \left[\breve{\delta}^-_{t'\alpha'} n_c(\boldsymbol{r}) \nabla_\alpha V_{eff}(\boldsymbol{r}) + n_c(\boldsymbol{r}) \nabla_\alpha \breve{\delta}^-_{t'\alpha'} V_{eff}(\boldsymbol{r}) \right] \tag{61}$$

C. Valence contribution to the dynamical matrix

Valence contribution is obtained similarly to obtaining the core contribution:

$$\sqrt{m_t m_{t'}} D^{val}_{t\alpha;t'\alpha'}(\boldsymbol{q}) = - \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \left[\breve{\delta}^- V^{t'\alpha'}_{eff}(\boldsymbol{r}) \nabla_\alpha n_{val}(\boldsymbol{r}) + V_{eff}(\boldsymbol{r}) \nabla_\alpha \breve{\delta}^- n^{t'\alpha'}_{val}(\boldsymbol{r}) \right] \tag{62}$$

D. Surface contribution to the dynamical matrix

Let us consider the contribution to the dynamical matrix from the surface term in (59).

$$\sqrt{m_t m_{t'}} D^{surf}_{t\alpha;t'\alpha'}(\boldsymbol{q}) = - \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \int_{S_t} \mathrm{d}S_\alpha \Big[\delta^-_{t'\alpha'} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) (\hat{H}_{kin} - E_\lambda(\boldsymbol{k})) \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int}$$
$$+ \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) (\hat{H}_{kin} - E_\lambda(\boldsymbol{k})) \breve{\delta}^-_{t'\alpha'} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int} \Big]$$
$$= (\text{changing } \boldsymbol{k} \leftrightarrow -\boldsymbol{k} \text{ in the first term and using the time-reversal symmetry})$$
$$- \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \{ \int_{S_t} \mathrm{d}S_\alpha \Big[\delta^-_{t'\alpha'} \Psi^T_\lambda(\boldsymbol{k},\boldsymbol{r}) (\hat{H}^*_{kin} - E_\lambda(\boldsymbol{k})) \Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int}$$
$$+ \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) (\hat{H}_{kin} - E_\lambda(\boldsymbol{k})) \delta^-_{t'\alpha'} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int} \Big] \tag{63}$$

Now let us consider the degenerate case $E_\mu(\boldsymbol{k}-\boldsymbol{q}) = E_\lambda(\boldsymbol{k})$. With the Eqn.(37) we will consider explicitly the $(-\boldsymbol{k}+\boldsymbol{q})$-term in the above equation and with μ-sum including only the degenerate levels:

$$
\begin{aligned}
D^{surf}_{t\alpha;t'\alpha'}(\boldsymbol{q}) = -\frac{1}{2}\sum_{\boldsymbol{k}\lambda}\sum_{\mu}\Big\{ & f_{\boldsymbol{k}\lambda}\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) - E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k}) - E_\mu(\boldsymbol{k}-\boldsymbol{q})} \\
& \times \int_{S_t} \mathrm{d}S_\alpha \Big[\Psi^T_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})(\hat{H}^*_{kin} - E_\lambda(\boldsymbol{k}))\Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int} \\
& +\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})(\hat{H}_{kin} - E_\lambda(\boldsymbol{k}))\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})|_{Int}\Big] \\
& + f_{-\boldsymbol{k}+\boldsymbol{q}\mu}\frac{\bar{H}^{t'\alpha'}_{\lambda\mu}(-\boldsymbol{k}+\boldsymbol{q}) - E_\mu(-\boldsymbol{k}+\boldsymbol{q})\bar{O}^{t'\alpha'}_{\lambda\mu}(-\boldsymbol{k}+\boldsymbol{q})}{E_\mu(-\boldsymbol{k}+\boldsymbol{q}) - E_\lambda(-\boldsymbol{k})} \\
& \times \int_{S_t} \mathrm{d}S_\alpha \Big[\Psi^T_\lambda(-\boldsymbol{k},\boldsymbol{r})(\hat{H}^*_{kin} - E_\mu(-\boldsymbol{k}+\boldsymbol{q}))\Psi^*_\lambda(-\boldsymbol{k}+\boldsymbol{q},\boldsymbol{r})|_{Int} \\
& +\Psi^\dagger_\mu(-\boldsymbol{k}+\boldsymbol{q},\boldsymbol{r})(\hat{H}_{kin} - E_\mu(-\boldsymbol{k}+\boldsymbol{q}))\Psi_\lambda(-\boldsymbol{k},\boldsymbol{r})|_{Int}\Big]\Big\} \\
= & \text{(making use of the time-reversal symmetry and property (40))} \\
-\sum_{\boldsymbol{k}\lambda}\sum_{\mu} f_{\boldsymbol{k}\lambda}\Big\{ & -\frac{1}{2}\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})\int_{S_t} \mathrm{d}S_\alpha \Big[\Psi^T_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})(\hat{H}^*_{kin} - E_\lambda(\boldsymbol{k}))\Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r})|_{Int} \\
& +\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})(\hat{H}_{kin} - E_\lambda(\boldsymbol{k}))\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})|_{Int}\Big] \\
& - \Big[\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) - E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})\Big]\int_{S_t} \mathrm{d}S_\alpha \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})|_{Int}\Big\} \qquad (64)
\end{aligned}
$$

The first integral in the above equation obtained simply from (63) if we replace the coefficient in (37) for the degenerate levels by $-\frac{1}{2}\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})$ as we already noticed after Eq.(45). The equation (64) thus states that there is an additional contribution from the degenerate levels as given by the last term in (64).

E. Band contribution to the dynamical matrix

Consider now the contribution to the dynamical matrix from the first two terms in (59). Using definition (31) and time-reversal symmetry, we can rewrite this first order variation as

$$
\begin{aligned}
\frac{\partial E^{band}_{tot}}{\partial Q_{t\alpha}} = \sum_{\boldsymbol{R}} \mathrm{e}^{-\mathrm{i}\boldsymbol{qR}}\sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda}\Big\{ & \int_{\Omega_t} \mathrm{d}\boldsymbol{r}\,\breve{\delta}^{+}_{t\alpha}\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \\
& \int_{\Omega_t} \mathrm{d}\boldsymbol{r}\,\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\breve{\delta}^{+}_{t\alpha}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})\Big\}
\end{aligned}
$$

$$= \sum_{\boldsymbol{R}} \mathrm{e}^{-\mathrm{i}\boldsymbol{qR}} \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Big\{ \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \breve{\breve{\delta}}^{+}_{t\alpha} \Psi^T_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H}^* - E_\lambda(\boldsymbol{k})]\Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r})$$

$$\int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\breve{\breve{\delta}}^{+}_{t\alpha}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \Big\} \tag{65}$$

Performing second variation we arrive to the band contribution to the dynamical matrix

$$\sqrt{m_t m_{t'}} D^{band}_{t\alpha;t'\alpha'}(\boldsymbol{q}) = \sum_{\boldsymbol{k}\lambda} f_{\boldsymbol{k}\lambda} \Big\{ \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Big[\breve{\delta}^{-}_{t'\alpha'} \breve{\breve{\delta}}^{+}_{t\alpha} \Psi^T_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H}^* - E_\lambda(\boldsymbol{k})]\Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r})$$

$$+\Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\breve{\delta}^{-}_{t'\alpha'}\breve{\breve{\delta}}^{+}_{t\alpha}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \Big] +$$

$$\int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Big[\breve{\breve{\delta}}^{+}_{t\alpha} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H} - E_\lambda(\boldsymbol{k})]\breve{\delta}^{-}_{t'\alpha'}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$$

$$+\breve{\delta}^{-}_{t'\alpha'}\Psi^T_\lambda(\boldsymbol{k},\boldsymbol{r})[\hat{H}^* - E_\lambda(\boldsymbol{k})]\breve{\breve{\delta}}^{+}_{t\alpha}\Psi^*_\lambda(\boldsymbol{k},\boldsymbol{r}) \Big]$$

$$+ \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \breve{\breve{\delta}}^{+}_{t\alpha} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) \breve{\delta}^{-}_{t'\alpha'} V_{eff} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$$

$$+ \int_{\Omega_t} \mathrm{d}\boldsymbol{r} \Psi^\dagger_\lambda(\boldsymbol{k},\boldsymbol{r}) \breve{\delta}^{-}_{t'\alpha'} V_{eff} \breve{\breve{\delta}}^{+}_{t\alpha} \Psi_\lambda(\boldsymbol{k},\boldsymbol{r}) \Big\}, \tag{66}$$

where

$$\breve{\delta}^{-}_{t'\alpha'}\breve{\breve{\delta}}^{+}_{t\alpha}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})|_t = \mathrm{i}\sum_{\boldsymbol{G}s}(k-q+G)_\alpha \delta^{-}_{t'\alpha'} A^{\boldsymbol{G}s}_\lambda(\boldsymbol{k})\Phi_A(\boldsymbol{k}-\boldsymbol{q}+\boldsymbol{G},s;\boldsymbol{r})$$

$$+\mathrm{i}(k-q)_\alpha \sum_n \delta^{-}_{t'\alpha'} B^{tn}_\lambda(\boldsymbol{k})\Phi^{tn}_B(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})$$

$$-\delta_{tt'}\Big[\sum_{\boldsymbol{G}s}(k+G)_\alpha(k+G)_{\alpha'} A^{\boldsymbol{G}s}_\lambda(\boldsymbol{k})\Phi_A(\boldsymbol{k}+\boldsymbol{G},s;\boldsymbol{r})$$

$$+k_\alpha k_{\alpha'} \sum_n B^{tn}_\lambda(\boldsymbol{k})\Phi^{tn}_B(\boldsymbol{k};\boldsymbol{r}) \Big] \tag{67}$$

Let us now consider the degenerate case. Special treatment is needed only for the first and second integrals in (66). And there is contribution only from the terms that contain the variation of the coefficients. Corresponding part of $\breve{\delta}^{-}_{t'\alpha'}\breve{\breve{\delta}}^{+}_{t\alpha}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$ is

$$\mathrm{i}\sum_{\boldsymbol{G}s}(k-q+G)_\alpha \delta^{-}_{t'\alpha'} A^{\boldsymbol{G}s}_\lambda(\boldsymbol{k})\Phi_A(\boldsymbol{k}-\boldsymbol{q}+\boldsymbol{G},s;\boldsymbol{r})$$

$$+\mathrm{i}(k-q)_\alpha \sum_n \delta^{-}_{t'\alpha'} B^{tn}_\lambda(\boldsymbol{k})\Phi^{tn}_B(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})$$

$$= \sum_\mu \frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k}) - E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k}) - E_\mu(\boldsymbol{k}-\boldsymbol{q})} \breve{\breve{\delta}}^{+}_{t'\alpha'}\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r}), \tag{68}$$

where we used (37) and (31). The part with singularity in $\breve{\delta}^{-}_{t'\alpha'}\Psi_\lambda(\boldsymbol{k},\boldsymbol{r})$ is

$$\sum_{\boldsymbol{G}s}\delta^{-}_{t'\alpha'}A^{\boldsymbol{G}s}_{\lambda}(\boldsymbol{k})\Phi_A(\boldsymbol{k}-\boldsymbol{q}+\boldsymbol{G},s;\boldsymbol{r})+\sum_{n}\delta^{-}_{t'\alpha'}B^{tn}_{\lambda}(\boldsymbol{k})\Phi^{tn}_{B}(\boldsymbol{k}-\boldsymbol{q};\boldsymbol{r})$$
$$=\sum_{\mu}\frac{\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})}{E_\lambda(\boldsymbol{k})-E_\mu(\boldsymbol{k}-\boldsymbol{q})}\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r}) \qquad (69)$$

Using (68) and (69), and similar to the consideration of degeneracy in the case of surface contribution, we obtain from (66) that 1)the coefficients at the degenerate levels in the expansion (37) must be replaced with $-\frac{1}{2}\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})$, and 2)there is an additional contribution:

$$-\sum_{\boldsymbol{k}\lambda}\sum_{\mu}f_{\boldsymbol{k}\lambda}\left[\bar{H}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})-E_\lambda(\boldsymbol{k})\bar{O}^{t'\alpha'}_{\mu\lambda}(\boldsymbol{k})\right]$$
$$\times\left[\int_{\Omega_t}d\boldsymbol{r}\Psi^{\dagger}_{\lambda}(\boldsymbol{k},\boldsymbol{r})\breve{\bar{\delta}}^{+}_{t\alpha}\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})+\int_{\Omega_t}d\boldsymbol{r}\breve{\bar{\delta}}^{+}_{t\alpha}\Psi^{\dagger}_{\lambda}(\boldsymbol{k},\boldsymbol{r})\Psi_\mu(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{r})\right] \qquad (70)$$

VI. CONCLUSIONS AND PLANS FOR THE FUTURE

In summary, the relativistic formulations of the ab-initio calculation of the atomic forces and the phonon spectra with full-potential linear-augmented-plane-wave method are presented in this report. The atomic forces, calculated for the α-Pu, have been used to estimate the effect of geometry relaxation on the ground state properties of α-Pu. The program code with the possibility of the calculation of the phonon spectra is now under testing. The results of these tests and the calculation of the phonon spectrum of α-U are planned to be included in the next report.

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